STUDIES OF HOMOGENEOUS AND HETEROGENEOUS HYDRAZINE DECOMPOSITION FOR MONOPROPELLANT PROPULSION SYSTEMS

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STUDIES OF HOMOGENEOUS AND HETEROGENEOUS HYDRAZINE
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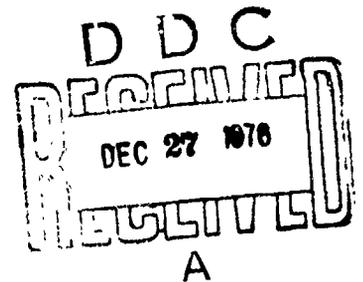
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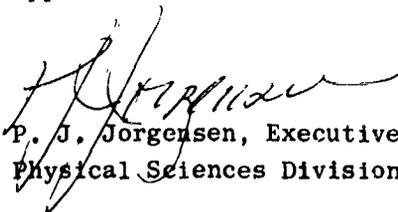
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Heterogeneous kinetic studies of hydrazine decomposition at atmospheric and subatmospheric pressures and infrared absorption measurements on alumina-supported iridium catalysts point to a reaction intermediate as the surface contaminant responsible for catalyst deactivation. The temperature region around 450 K has been found to be most detrimental to catalyst life under laboratory test conditions for hydrazine decomposition.

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1 INTRODUCTION

For several years, considerable effort has been devoted to developing a N_2H_4 fueled monopropellant control thruster capable of reliable and prolonged operation in a space environment. Current monopropellant engines use a Shell-405 catalyst bed (an alumina-supported iridium catalyst) to decompose liquid hydrazine into hot gaseous products. However, during repetitive operation of such engines in a limited pulse mode cycle, the catalytic reactor exhibits a gradual loss of thrust generally attributed to a deterioration in catalyst performance. Ultimately "washout" occurs, a process in which liquid N_2H_4 penetrates through the catalyst bed without decomposition.

The mechanisms by which loss in catalyst activity are thought to occur can generally be separated into two categories:

- The physical breakup of the catalyst caused by either thermal shocks over the large temperature range experienced during operation, or large pressure gradients generated within the catalyst particle resulting from pore wetting by liquid reactant.

- Catalyst poisoning, i.e., the adsorption of surface species on a significant part of the catalyst surface.

Earlier studies of the mechanism of hydrazine decomposition on evaporated film of tungsten and molybdenum[1,2] have indicated that N-H and N-N bonds break during the catalytic decomposition of N_2H_4, with different mechanisms and products prevailing at high and low temperatures. Our studies with polycrystalline Ir[3] and alumina-supported Ir crystallites[4] (Shell-405) have identified the presence of hydrogen and nitrogen adatoms

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with several distinct binding states on the surface of the metal. Our results suggest that strongly bound nitrogen adspecies formed during N_2H_4 decomposition can contribute to the loss of catalyst activity encountered during H_2H_4 exposure.

During the current program year, we have studied in detail the mechanism of surface adsorbate formation, with the objectives of: (1) relating catalyst activity decline to N_2H_4 exposure at different temperatures, (2) determining N_2H_4 and NH_3 decomposition kinetics at low pressures in the absence of concentration and temperature gradients in the reactor, and (3) identifying by infrared absorption studies the surface intermediates responsible for catalyst deactivation.

Section II describes our experimental approach to these studies, in Sections III and IV we present and discuss our results. Our conclusions are set forth in Section V.

II EXPERIMENTAL DETAILS

A. Atmospheric Pressure Reactor

A powdered sample of catalyst (5.5×10^{-3} g of 10 wt% Ir/Al_2O_3),
was placed in a differential flow reactor and exposed to a stream of
gaseous hydrazine. The reactant stream ($\sim$ 2 vol% N_2H_4, 98 vol% He)
was generated by bubbling He through liquid N_2H_4 (Olin Technical Grade)
at room temperature, followed by additional He dilution. After a
specified length of exposure at elevated temperatures, the catalyst was
examined for activity by passing over it a pulse of N_2H_4 vapor (6.3×10^{-6}
moles) in a He carrier stream at 300 K. The degree of N_2H_4 conversion
was determined by gas chromatographic analysis of the mass of N_2 formed.
This measurement accurately describes catalyst activity, since only NH_3
and N_2 are products of the decomposition at 300 K. Before admission of
the sample to the gas chromatograph, we removed NH_3 and unreacted N_2H_4
from the product stream by condensation in a cold trap (cooled by liquid
nitrogen) to avoid interference with the N_2 measurement.

B. Low Pressure Reactor

Two fused-silica reactors were used. Both were operated under
Knudsen flow conditions where the mean-free path of the reactant
molecules is greater than the diameter of the catalyst pellet and
the reactor exit aperture. The first reactor (R1, Figure 1) was a
cylindrical quartz chamber into which several catalyst pellets of
Shell-405 were placed. A gas mixture composed of gaseous hydrazine and
inert gas (argon) enters the reactor. A mass spectrometer is used to

continually sample the product mixture flowing through the exit aperture. The fractional decomposition of reactant is determined by comparing mass spectral signals of product to reactant and inert gas. Reactor R1 was used for most of the studies with the exception of the measurements of low-temperature catalyst deactivation by N_2H_4 (300 K $<$ T $\lesssim$ 550 K), for which Reactor R2 (Figure 2) was used.

Reactor R2 consists of two chambers separated by a valve. The gas flows into a quartz chamber with an exit aperture. The gas flow can be directed to a neighboring, catalyst-containing chamber by operating the externally activated valve. Since the conductance of the open valve is much larger than that of the exit aperture, the two chambers are effectively unified. The fractional disappearance of reactant may be directly measured by monitoring reactants with the valve open and closed, thereby exposing and bypassing the catalyst. The relative conversion of reactant may thus be determined without reference to a calibration signal for the inert carrier gas. For analysis, the gases exiting from the reactor are formed into a molecular beam, which is chopped with a rotating chopping wheel and mass spectrometrically detected by use of phase-sensitive electronics. This detection system (Figure 3) ensures that the gas mixture flowing from the reactor is monitored before adsorption and reaction downstream of the reactor.

The technique is termed very low pressure pyrolysis (VLPP) and is fully described in Reference 5. If a species, B, can react by a first-order reaction or effuse from the reactor, we have the simple pseudo-chemical system:

$$B \xrightarrow{k_d} \text{products} \tag{1}$$

$$B \xrightarrow{k_e} \text{effusion} \tag{2}$$

Under Knudsen conditions (stirred flow-reactor), we have

$$k_e = \frac{\bar{C}A_e}{4V}$$; where $\bar{C}$ is the mean velocity,

A_e is the aperture area, and

V is the volume of the reactor.

$$k_d = P_c k_c = \frac{P_c \bar{C}A_e}{4V}$$; where P_c is the reaction probability

per collision with the external

surface of the catalyst A_c

The rate constants k_e and k_d refer to Equations (1) and (2).
In the absence of catalytic reaction the average concentration of
reactant in the reactor is given by:

$$(B)_o = F_B/k_e V,$$ where F_B is the flux of B into the reactor.

In the presence of catalyst,

$$(B) = \frac{F_B}{(k_e + k_d)V}$$,

Thus,

$$\frac{(B)_o}{(B)} = \frac{k_e + k_d}{k_e} = 1 + \frac{k_d}{k_e}$$,

and

$$\frac{(B)_o - (B)}{(B)} = \frac{k_d}{k_e} = \frac{P_c k_c}{k_e} = P_c \frac{A_c}{A_e}$$.

Therefore,

$$P_c = \frac{A_e}{A_c} \frac{(B)_o - (B)}{(B)} \tag{3}$$

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If we define the fraction decomposed as

$$f_d \equiv \frac{(B)_o - (B)}{(B)_o}$$

then,

$$P_c = \frac{A_e}{A_c}\left(\frac{f_d}{1 - f_d}\right) \qquad (4)$$

It can be shown that if P_c is independent of F_B, the process is first-order. Otherwise, its order dependence must be determined. For Knudsen flow in our apparatus, the gas pressures used are in the 10^{-3} torr range.

C.   Infrared Studies

1.   Description of Apparatus

The 10-cm Pyrex infrared cell used for this study is "T" shaped[6] as shown in Figure 4. The outside of the vertical section is wrapped with resistance wire and provided with a thermowell for temperature measurement. The end plates of the horizontal section of the cell are equipped with NaCl windows. The catalyst is deposited on a BaF_2 crystal which can be raised and lowered into the vertical section of the cell by means of a specially designed Teflon stopcock provided with a Pyrex string attached to the crystal. For ir measurements the crystal is lowered into the horizontal window section before and after exposure to gases at elevated temperatures or during exposure to gaseous reactants or inert carrier gas (He or Ar) at room temperature. Infrared spectra are obtained during flow conditions at 1 atmosphere total pressure with a Perkin-Elmer Model 457 spectrometer. With the catalyst samples under study, good spectral transmission was achieved in the frequency region 4000 to 1200 cm^{-1}. A scan over this spectral region is sufficient to detect most of the reported OH and NH vibrational frequencies. Hydrazine

is vaporized by bubbling He at a slow rate through a liquid sample to give a saturated vapor stream ($\sim$ 2 vol%), which is subsequently diluted with additional He to $\sim$ 1 vol% before it enters the cell.

2. Catalyst Preparation

The catalyst is prepared by depositing five 0.05 cm^3 aliquots of an aqueous dispersion of $IrCl_4$ in colloidal Al_2O_3 (Baymal) on each side of the BaF_2 crystal (8 x 8 x 25 mm). Each aliquot is spread to wet the entire optical surfaces and is then evaporated to dryness with an ir heat lamp before the next aliquot is added. By this technique, 3 mg of $\sim$ 10 wt% Ir on Al_2O_3 can be dispersed. This technique was also used to prepare a blank containing only Al_2O_3. Before study, the catalyst was reduced in H_2 at 723 K for 30 min, flushed in He at 723 K for 10 min, then cooled to room temperature.

III   RESULTS

A.   High-Pressure Studies

A gradual decay in catalytic conversion of N_2H_4 was detected for an Ir/Al_2O_3 catalyst sample exposed to N_2H_4 in a He carrier stream at various temperatures, and subsequently examined for activity in a pulse mode at 300 K. The rate of decay appeared to be a sensitive function of catalyst temperature (Figure 5). The highest degree of catalyst deactivation occurred near 450 K (Figure 6). This deactivation could be partially reversed by heating the catalyst in a He carrier stream. However, temperatures above 673 K were required to approach the initial level of activity (Table 1), indicating that a strongly bound adspecies may be the cause of catalyst poisoning under our experimental conditions.

To determine the influence of the pore structure of Shell-405 catalyst in N_2H_4 decomposition, we compared the loss in catalytic activity of pelletized and powdered samples (Figure 7). The pelletized sample exhibited a much more rapid decline in catalytic activity than did the powdered sample. The Ir crystallite within the internal pore structure of the pellet obviously can not participate to any large extent in the N_2H_4 decomposition reaction.

B.   Low-Pressure Studies

We have found two distinctly different temperature regimes of N_2H_4 decomposition on Ir/Al_2O_3:   in the range above approximately 600 K, a reproducible exposure-independent decomposition is observed; below 550 K, an exposure-dependent decomposition with rather complex kinetics

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is noted. Ammonia decomposition to N_2 and H_2 is detectable above approximately 600 K.

The following reaction, independent of the N_2H_4 exposure, was found to prevail at temperatures greater than 600 K (Figure 8):

$$N_2H_4 \rightarrow NH_3 + 1/2 \ N_2 + 1/2 \ H_2 \qquad (5)$$
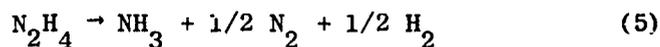
The activation energy, E_{act}, was found to be 2.2 ± 0.3 kcal mol^{-1}. Below 550 K, ammonia and nitrogen are the only products of N_2H_4 decomposition in accordance with the stoichiometry:

$$3 \ N_2H_4 \rightarrow 4 \ NH_3 + N_2 \qquad (6)$$
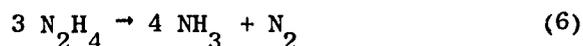
on both active and partially poisoned Ir/Al_2O_3. Active catalyst surfaces could be generated by heating to 1000 K in H_2. The activity was determined before measurable poisoning caused by exposure to N_2H_4 at temperatures below 600 K. As shown by the data in Figure 9, activity reaches a minimum near 425 to 450 K, and its temperature dependence in this region cannot be fitted by a single arrhenius expression. The initial reaction probability is high (> 0.1 collision^{-1}); however, because of the strong dependence of activity on exposure to technical grade hydrazine, our study of the initial activity has been limited. Also small pressure dependence was noted for this reaction over the temperature range 298 to 873 K both for fresh and partially poisoned catalyst samples (Figure 10).

The catalytic decomposition of NH_3 to N_2 and H_2 was found to occur on Ir/Al_2O_3 catalyst above 600 K (Figure 11). On two catalyst samples of somewhat differing activity the rate of NH_3 decomposition was found to be approximately one-tenth the rate for N_2H_4 decomposition (Figure 12). Although more careful analyses of the flow and temperature dependence

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of the relative rate of the NH_3 reaction versus the N_2H_4 reaction was needed, the NH_3 reaction appears to be a convenient, albeit an indirect, probe for activity evaluation of the catalyst.

In agreement with the high-pressure studies discussed in the preceding section, a gradual decay in catalyst activity was noted on exposure to technical grade hydrazine below 600 K. Typical results are shown in Figure 13. Exposing such a poisoned catalyst to a flow of H_2 at low temperatures, or leaving the catalyst in the reactor for several days does not restore initial activity. However, heating above 700 K completely rejuvenated the catalyst. In addition, the activity of catalyst poisoned at room temperature could be temporarily restored by heating to 400 K (approximately 80% of the initial activity). However prolonged exposure at 400 K resulted in poisoning.

With Reactor R2, we have noted an interesting and potentially important aspect of N_2H_4 decomposition on exposure-poisoned Ir/Al_2O_3. The onset of N_2 and NH_3 product appearance follows N_2H_4 exposure with a delay time that increases monotonically with exposure poisoning. If this delay, $\tau_d(298 \text{ K})$, is defined as the time interval between N_2H_4 exposure at 298 K (valve in R2 is opened to begin exposure to the catalyst) and appearance of products, then for unpoisoned catalyst, $\tau_d(298 \text{ K})$ is approximately 1 to 3 sec, whereas for a catalyst poisoned by N_2H_4 exposure to 50% of this initial activity, $\tau_d(298 \text{ K})$ is approximately 15 to 30 sec (Figure 14).

Exposure of Ir/Al_2O_3 pellets to CO at 298 K was found to reduce catalytic activity for N_2H_4 decomposition. Figure 15 shows such deactivation for fresh and partially N_2H_4-exposure poisoned catalyst. The initial rapid deactivation may result either from poisoning of the most accessible active sites near the surface or from selective poisoning on specially susceptible reaction sites.

At 800 K, exposure to toluene was found to cause catalyst deterioration. Activity was reduced by roughly one-half after exposure to approximately 10^{19} molecules at this temperature. Additional quantities of toluene had little further effect on activity. In this regard, this poisoning effect is similar to N_2H_4 and CO-induced deactivation at lower temperature. At 900 K, O_2 exposure was found to completely restore the activity. Most likely, the carbon deposited on the surface by toluene decomposition reacts to form CO which readily desorb at this high temperature.[7]

C. Infrared Studies

Figure 16 shows a typical infrared spectrum obtained for the Ir/Al_2O_3 catalyst and the Al_2O_3 blank after 16 hours exposure to N_2H_4 ($\sim 6 \times 10^{-3}$ moles). Although the magnitude of absorption-band intensities can only be evaluated semiquantitatively because small peak-overlap corrections have not been made, the bands observed can be assigned to OH, NH, and NH_2 absorption frequencies in addition to molecularly adsorbed N_2H_4 and NH_3 (Table 2). While many of the absorption bands are common to both the Al_2O_3 support ("blank") and the Ir/Al_2O_3 catalyst, the absorption bands at 1499 and 1469 cm^{-1} are found only on Ir/Al_2O_3. These absorption bands can be assigned to frequencies characteristic of NH_2^+ and NH_4^+ species, respectively. Comparison of the spectra observed for Ir/Al_2O_3 exposed to N_2H_4 and to NH_3 indicates that the band at 1499 cm^{-1} is formed only during N_2H_4 exposure, whereas the 1469 cm^{-1} band appears associated with both NH_3 and N_2H_4 (Table 2). Exposures of the Al_2O_3 support to N_2H_4 and NH_3 result in spectra in which the bands at 1499 and 1469 cm^{-1} are absent. The band at 1623 cm^{-1} appears to be characteristic of OH or adsorbed molecular N_2H_4. From a comparison of data given in Table 2, the ir spectrum of N_2H_4-exposed Ir/Al_2O_3 can be simplified in terms of specific surface assignments. As shown

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in Table 3, the ir bands at $\sim$ 3474, 1623, and 1603 cm^{-1} are associated with the Al_2O_3 surface, and those at 1499 and 1469 cm^{-1}, with the Ir surface.

All bands, except those at $\sim$ 3474 cm^{-1} (OH) and 1469 cm^{-1} (NH_4^+), are observed to increase with N_2H_4 exposure (Table 4). The bands showing the largest intensity increase are located at 1603 cm^{-1} (N_2H_4/Al_2O_3) and at 1499 cm^{-1} (NH_2/Ir).

Over a range of exposures to N_2H_4, significant changes in peak intensities occur for bands associated with N_2H_4, NH_3 (3335 cm^{-1}), N_2H_4 (1603 cm^{-1}), and NH_2 (1499 cm^{-1}) frequencies (Figure 17). From the initial slope of the data shown, we estimate the rate of formation of the N_2H_4/NH_3 band to be about a factor of 2 greater than that for the N_2H_4 and NH_2 bands. Kinetic analysis of the formation of these bands can be made from the typical Langmuir type of first and second order rate laws

$$d\theta/dt = k(1-\theta) \tag{7}$$

and

$$d\theta/dt = k(1-\theta)^2 \tag{8}$$

where θ = fractional monolayer coverage

Integration of Equations (7) and (8) between the limits 0 to θ provides the expressions

$$kt = -\ln(1-\theta) \tag{9}$$

and

$$kt = \theta/1-\theta \tag{10}$$

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Using the data given in Figure 17 to obtain values for θ, we find that Equations (9) and (10) can be used to interpret the formation of the 3335, 1603, and 1499 cm^{-1} bands. The band at 1499 cm^{-1} (NH_2/Ir) is found to be of second order in the unoccupied site density, s, on the metal surface, i.e., $N_2H_4 + 2s \rightarrow 2$ (NH_2-s). The other two follow first-order kinetics (Figure 18).

The relative binding strengths of the surface adsorbates seen by ir spectroscopy can be deduced from measurements of the change in absorbance as a function of temperature in a He carrier stream. The results (Table 5) indicate that at 373 K, all the band intensities are reduced to near background levels, except those at 1603 cm^{-1} (N_2H_4/Al_2O_3), 1499 cm^{-1} (NH_2/Ir), and 1469 cm^{-1} (NH_4^+/Ir). The last two band intensities show the smallest changes over the entire temperature range studied. Exposure of the catalyst to N_2H_4 at room temperature yields an absorption spectrum comparable to that seen before heating in He.

When Ir/Al_2O_3 is exposed to N_2H_4/H_2 rather than to N_2H_4/He, the general appearance of the absorption spectrum is the same. But the absolute intensities of the bands at 1499 cm^{-1} and 1469 cm^{-1} are reduced considerably, whereas those of the other bands are of comparable magnitude or somewhat larger (Table 6).

IV DISCUSSION

Earl$^\cdot$$^\cdot$r studies[4] with Shell-405 catalyst indicated that an adsorbate remained on the catalyst surface following exposure to pulses of hydrazine. The surface-adsorbed species were chemically identified and their binding energies to the catalyst surface deduced by temperature-programmed desorption (TPD).[4] One of the most strongly bound species was found to yield gaseous nitrogen, $N_2(\beta_2)$, after the Ir/Al_2O_3 catalyst reached a temperature of about 675 K. The studies indicated that the $N_2(\beta_2)$ could originate from adspecies involving such precursors as NH_2 and NH formed by rupture of the N-N bond during hydrazine adsorption. Auger electron spectroscopy did indeed show nitrogen adspecies to be present on catalyst samples removed from operational thrusters.[7] The question then arises if the buildup of surface species leads to the gradual decrease in Ir sites active for N_2H_4 decomposition on Shell-405 catalyst. The experimental results from this year's study further substantiate that reaction intermediates are one of the causes of catalyst deactivation in the $Ir-N_2H_4$ system.

Kinetic measurements at low pressure demonstrate that temperature is important in the product distribution. Below 550 K, hydrazine decomposes to N_2 and NH_3 almost exclusively [Equation (5)], whereas above 600 K, the products of the reaction [Equation (6)] are NH_3, N_2, and H_2. These data are in good agreement with earlier results[4] on the product distribution as a function of temperature at atmospheric pressure. In this work, however, no NH_3 was detected as a high-temperature product. Probably, under atmospheric pressure conditions the higher collison frequency led to NH_3 decomposition.

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Our results and the current data indicate that the mechanism of hydrazine decomposition on Shell-405 is of zero order in N_2H_4 pressure. In addition, both decomposition paths require very low activation energies. Smith and Solomon[8] report a value of nearly zero, compared with our value of 2.2 ± 0.3 kcal mol^{-1} for the high-temperature reaction [Equation (5)]. At high temperatures we have observed that the pre-exponential term (equivalent to reaction probability per collision) varies with the specific catalyst sample. The catalyst sample obtained from Rocket Propulsion Laboratory (RPL) exhibits much higher activity for N_2H_4 decomposition (that is, a higher preexponential factor) than the sample obtained from Rocket Research Corporation (RRC). These results may be related to variations in Ir metal surface area for the two samples. Indeed, measurement of metal dispersion by our CO-O titration technique[9] indicates that the fresh RPL catalyst has a surface area of 185 m^2/g Ir whereas the fresh RRC catalyst has a surface area of 154 m^2/g Ir. However, the observed variation in activity (a factor of 10) is greater than can be accounted for by the difference in metal dispersion (a factor of 1.2). Also, in a study with selected large pellets from the RPL sample, considerably lower activity was observed than for a random sample. More experimentation is needed to determine the reproducibility of catalyst activity for individual pellets.

Results obtained during low pressure poisoning studies demonstrate a delay in appearance of N_2H_4 decomposition products that increases monotonically with exposure. This effect has also been observed qualitatively during high pressure studies and suggests that the increase in time is associated with N_2H_4 diffusion into the interior of the catalyst pellet. The important role of pore diffusion in catalyst deactivation is further suggested by the results obtained in high pressure studies (1 atm), which demonstrated a significant effect of the particle size of the catalyst on its rate of deactivation (Figure 7).

In this work, a powdered sample of Shell-405 having a fraction of its pore structure destroyed during grinding is observed to poison less rapidly than Shell-405 in pelletized form. Additional studies are needed to fully understand the relationship between pore diffusion and catalyst deactivation.

We have observed experimentally that exposure of Shell-405 to carbon monoxide and to toluene reduces catalytic activity for N_2H_4 decomposition. These experiments showed that catalytic activity cannot be completely destroyed by long exposure to these materials. For the CO-exposed catalyst, the original activity can be restored by heating above 900 K. These data are in agreement with earlier TPD studies[8] that showed a desorption maximum for CO near this temperature. Toluene acts as a poison on Shell-405, presumably through carbon deposition, since treatment in O_2 at $\sim$ 900 K is required to restore original activity. These results suggest that hydrocarbon and CO impurities in the N_2H_4 fuel do not completely deactivate the catalyst.

A significant observation made during poisoning studies, at both low and atmospheric pressure, is the effect of temperature on catalyst deactivation. As shown in Figure 5, a maximum in catalyst deactivation is observed near 450 K, close to the temperature found in low pressure studies. The temperature pattern of catalyst poisoning follows closely the rate of desorption of surface-adsorbed hydrogen (α-hydrogen), an intermediate detected in temperature-programmed desorption studies[4] of the adsorbate retained by the catalyst after exposure to N_2H_4 (Figure 6). Mechanistically, we conclude that because of the rapid depletion of H-adatoms by recombination and H_2 desorption at 450 K, the $NH_2(s)$ surface intermediate formed in N_2H_4 decomposition,

$$N_2H_4 \rightarrow 2NH_2(s) \qquad\qquad (11)$$

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can undergo further dehydrogenation to strongly bound nitrogen adatoms $N(s)$:

$$NH_2(s) \rightarrow NH(s) + H(s) \qquad (12)$$

$$NH(s) \rightarrow N(s) + H(s) \qquad (13)$$

$$2H(s) \rightarrow H_2 \qquad (14)$$

rather than ammonia formation by:

$$NH_2(s) + H(s) \rightarrow NH_3(g) \qquad (15)$$

Only at temperatures above 450 K the reaction $2N(s) \rightarrow N_2$ takes place. Based on such a mechanism, one would conclude that in the presence of H_2 the deactivation process is modified. Such an effect has actually been observed. As shown on Figures 6 and 19, the decline of Shell-405 activity is substantially reduced in the presence of H_2. Low-pressure studies indicate that heating a partially deactivated catalyst in H_2 is effective in restoring a large fraction ($\sim$ 80%) of the initial activity.

Catalyst reactivation by exposure to He at elevated temperature demonstrates that temperatures above 673 K are required to restore the initial activity for hydrazine decomposition (Table 1). Similar results were obtained in low pressure studies. This observation is consistent with the presence of NH adspecies, which desorb[4] with N_2 and H_2 as products at temperatures above 673 K.

These kinetic results, in agreement with ir data, suggest that NH_2 adspecies on the surface of the Ir crystallites are the precursors to catalyst poisoning. Their removal requires reaction with H-adatoms to form NH_3 or high temperature desorption (> 675 K) with N_2 and H_2 as

products. In the latter case, however, the formation of strongly bound N-adatoms may lead to irreversible deactivation of the Ir surface (nitride formation) as observed in catalyst samples removed from thrusters.[6]

V CONCLUSION

Our results on N_2H_4 decomposition catalyzed by Ir/Al_2O_3 as derived from a combination of experimental techniques (kinetic studies at high and low pressures and infrared measurements) point to the presence of a reaction intermediate, as the surface contaminant likely to be responsible for Ir/Al_2O_3 deactivation. The data obtained from these studies indicate that the temperature region around 440 K is most detrimental to long-term operation of a hydrazine monopropellant fuel thruster because of the maximum rate of NH_2 adspecies buildup on the catalyst observed at this temperature. At somewhat higher temperatures, catalyst activity is less severely affected by this surface species because it undergoes progressive dehydrogenation and eventual desorption as N_2 and H_2. Based on these results, we would predict that longer catalyst life might be achieved by continuous operation at temperatures above 673 K. However, irreversible processes leading to the formation of a surface metal nitride and sintering of the catalyst may contraindicate long exposures at excessively high temperatures.

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Table 1

REACTIVATION OF Ir/Al_2O_3 CATALYST IN
He AT VARIOUS TEMPERATURES*

Temperature °K	Fractional N_2H_4 Conversion (%)[†]
297	0.40[‡]
472	0.51
573	0.55
673	0.61
724	0.98

*5.5×10^{-3} g of Ir/Al_2O_3 (10 wt%); heating time = 20 min.

[†]Measured at 298 K on exposure to pulse of N_2H_4 (6.3×10^{-6} moles).

[‡]After exposure to 16.8 moles N_2H_4/g in temperature range 371 to 623 K.

Table 2

SUMMARY OF IR SPECTRA OBSERVED ON
Ir/Al_2O_3 and on Al_2O_3 EXPOSED TO N_2H_4 or NH_3[*]

Band (cm^{-1})	(Assign)	Ir/Al_2O_3		Al_2O_3	
		N_2H_4	NH_3	N_2H_4	NH_3
∼ 3474	OH	VS, B	m, B	M, B	M, B
∼ 3335	N_2H_4, NH_3	VS, B	S, B	S, B	S, B
∼ 3177	NH	VS, B	S, B	M, B	M, B
1688	NH_3	A	W	A	A
1623	OH, N_2H_4	M	A	M	A
1603	N_2H_4	S	A	M	M
1588	NH_3	A	M	A	A
1549	NH	A	A	W	A
1499	NH_2	M	A		
1469	NH_4^+	W	M	A	A
1360		A	A	A	W
1261-1271	NH_3	W	W	W	W

[*] N_2H_4 ⋅ NH_3 Exposure = 6.0 x 10^{-3} moles at 295 K

VS = very strong

S = strong

M = medium

W = weak

A = absent

B = broad

Table 3

SPECIFIC SURFACE ASSIGNMENTS FOR
INFRARED BANDS FOUND ON N_2H_4 - EXPOSED Ir/Al_2O_3

Band (cm^{-1})	Assignment/Surface
~ 3474	OH/Al_2O_3
1623	OH/Al_2O_3
1603	N_2H_4/Al_2O_3
1499	NH_2/Ir
1469	NH_4^+/Ir

Table 4

EFFECT OF N_2H_4 EXPOSURE ON INFRARED BANDS OBSERVED ON Ir/Al_2O_3

Band (cm^{-1})	N_2H_4 Exp. mol x 10^3 Absorbance (log I_o/I)					% Band Change
	0.8	6.2	7.4	10.4	34.2	
~3474	0.47	0.35	0.39	0.29	0.38	-19
~3335	0.53	0.57	-	0.60	0.71	+34
~3177	0.48	0.50	0.51	0.50	0.63	+31
1623	0.17	0.21	0.22	0.28	0.30	+76
1603	0.12	0.30	0.28	0.38	0.36	+200
1549	-	-	0.09	0.11	0.11	+22
1499	0.09	0.15	0.14	-	0.21	+133
1469	0.09	0.05	0.04	0.05	0.08	-11
1261-1271	0.02	0.05	0.02	0.06	0.03	+50

Table 5

EFFECT OF HEATING IN He* ON ABSORPTION SPECTRUM OF
Ir/Al$_2$O$_3$ EXPOSED TO HYDRAZINE[†]

Band (cm^{-1})	Absorbance (log I$_o$/I)				
	Temperature (K)				
	295	373	473	573	725
$\sim$ 3474	0.32	$\sim$ 0	$\sim$ 0	$\sim$ 0	$\sim$ 0
$\sim$ 3335	0.39	$\sim$ 0	$\sim$ 0	$\sim$ 0	$\sim$ 0
$\sim$ 3177	0.35	$\sim$ 0	$\sim$ 0	$\sim$ 0	$\sim$ 0
1623	0.12	0.04	$\sim$ 0	$\sim$ 0	$\sim$ 0
1603	0.21	0.10	0.03	0.03	0.03
1499	0.15	0.12	0.08	0.05	0.04
1469	0.05	0.04	0.03	0.03	0.02
1261-1271	0.05	0.01	0.01	$\sim$ 0	$\sim$ 0

*For 15 minutes at He flow rate of 30 cc/min

[†]6.0 x 10^{-3} moles at 295 K

Table 6

EFFECT OF H_2 ON THE INFRARED SPECTRUM OF N_2H_4-EXPOSED Ir/Al_2O_3*

Band (cm^{-1})	Absorbance ($\log I_o/I$)	
	N_2H_4/He	N_2H_4/He/H_2
~ 3474	0.35	0.36
~ 3335	0.57	0.69
~ 3177	0.50	0.57
1623	0.21	0.24
1602	0.30	0.30
1499	0.15	0.08
1469	0.05	0.01
1261-1271	0.05	0.05

*Total N_2H_4 exposure = 6.0×10^{-3} moles; gas composition = 1 vol% N_2H_4/43 vol% H_2/56 vol% He.

P $\leq 10^{-3}$ torr

EXIT APERTURE

PRODUCTS

MOLECULAR
BEAM MASS
SPECTROMETRIC
DETECTION

N$_2$H$_4$(NH$_3$)

HEATER

SHELL-405
(~10^{-2} gm)

PUMPING

SA-2716-47

N$_2$H$_4$ FLOW RATE IN = N$_2$H$_4$ FLOW RATE OUT + N$_2$H$_4$ DECOMPOSITION RATE
AT LOW PRESSURE (MEAN FREE PATH > PELLET DIAMETER)

$$\text{REACTION PROBABILITY PER COLLISION WITH CATALYST EXTERIOR} = \frac{\text{EFFECTIVE EXIT AREA}}{\text{EFFECTIVE EXTERNAL CATALYST AREA}} \left(\frac{\text{FRACTION DECOMPOSED}}{\text{FRACTION REMAINING}} \right)$$
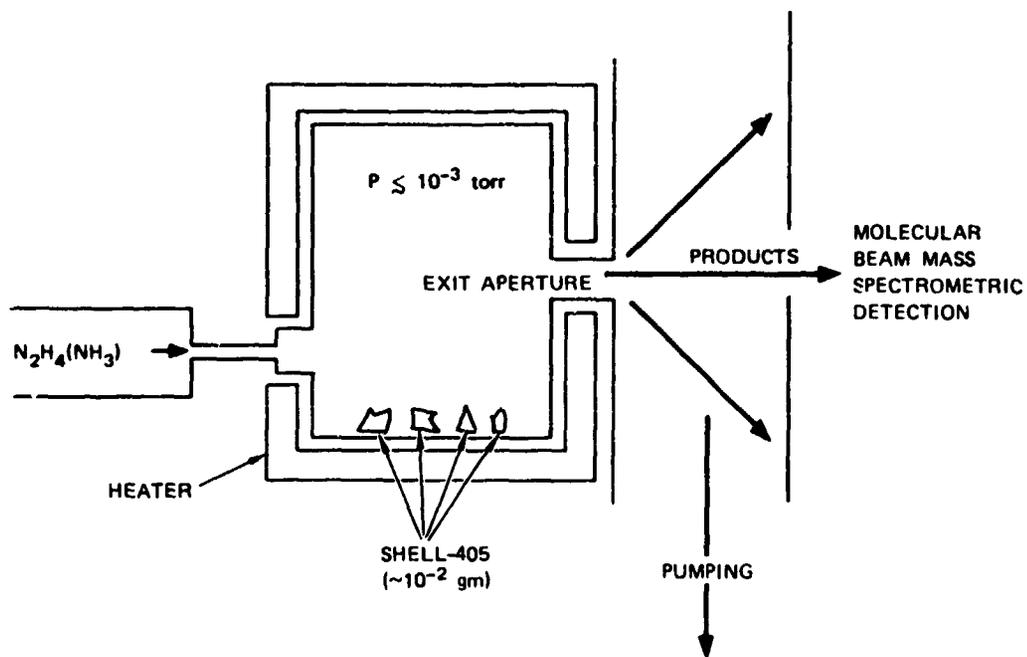
FIGURE 1   KNUDSEN FLOW REACTOR (R1) FOR MEASURING RATE OF N$_2$H$_4$
DECOMPOSITION ON SHELL-405 CATALYST

MAGNETICALLY
ACTUATED VALVE

REMOVABLE CATALYST
HOLDER

GAS INLET

REMOVABLE APERTURE
CONSTRICTOR

GAS OUTLET
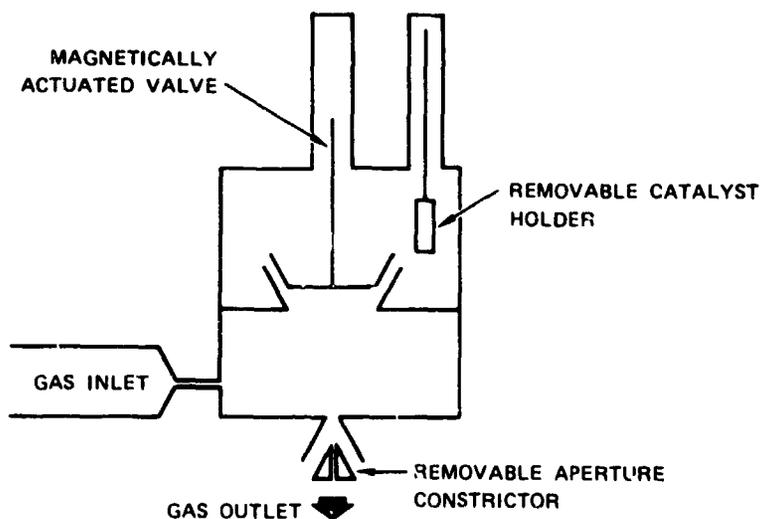
SA-2716-39

FIGURE 2   FUSED SILICA DUAL-CHAMBER LOW PRESSURE
FLOW REACTOR (R2)
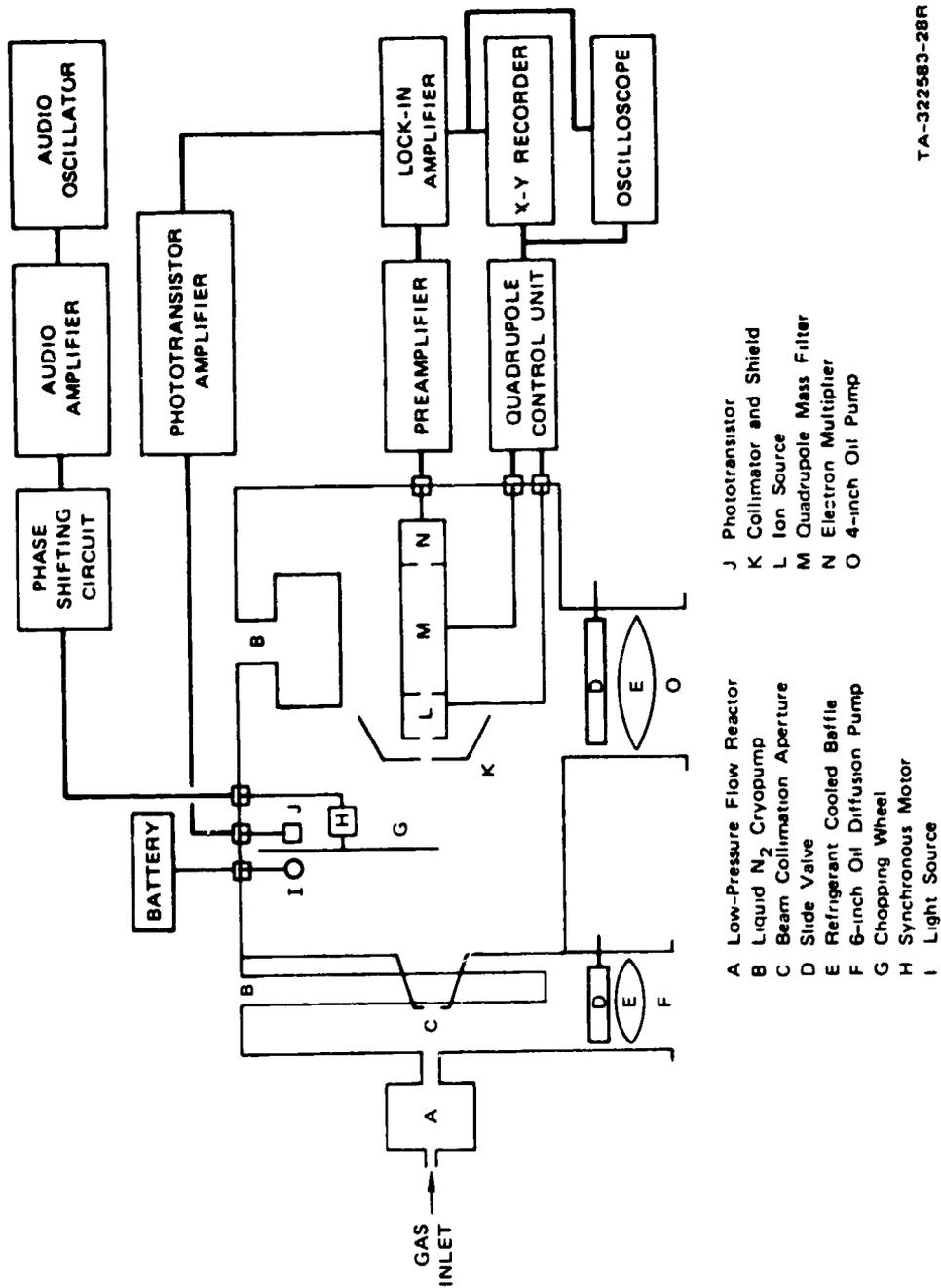
FIGURE 3   SCHEMATIC DIAGRAM OF DIFFERENTIALLY-PUMPED MODULATED-MOLECULAR-BEAM MASS
SPECTROMETRIC DETECTION SYSTEM FOR LOW PRESSURE FLOW REACTOR

A   Low-Pressure Flow Reactor
B   Liquid N_2 Cryopump
C   Beam Collimation Aperture
D   Slide Valve
E   Refrigerant Cooled Baffle
F   6-inch Oil Diffusion Pump
G   Chopping Wheel
H   Synchronous Motor
I   Light Source

J   Phototransistor
K   Collimator and Shield
L   Ion Source
M   Quadrupole Mass Filter
N   Electron Multiplier
O   4-inch Oil Pump

TA-322583-28R
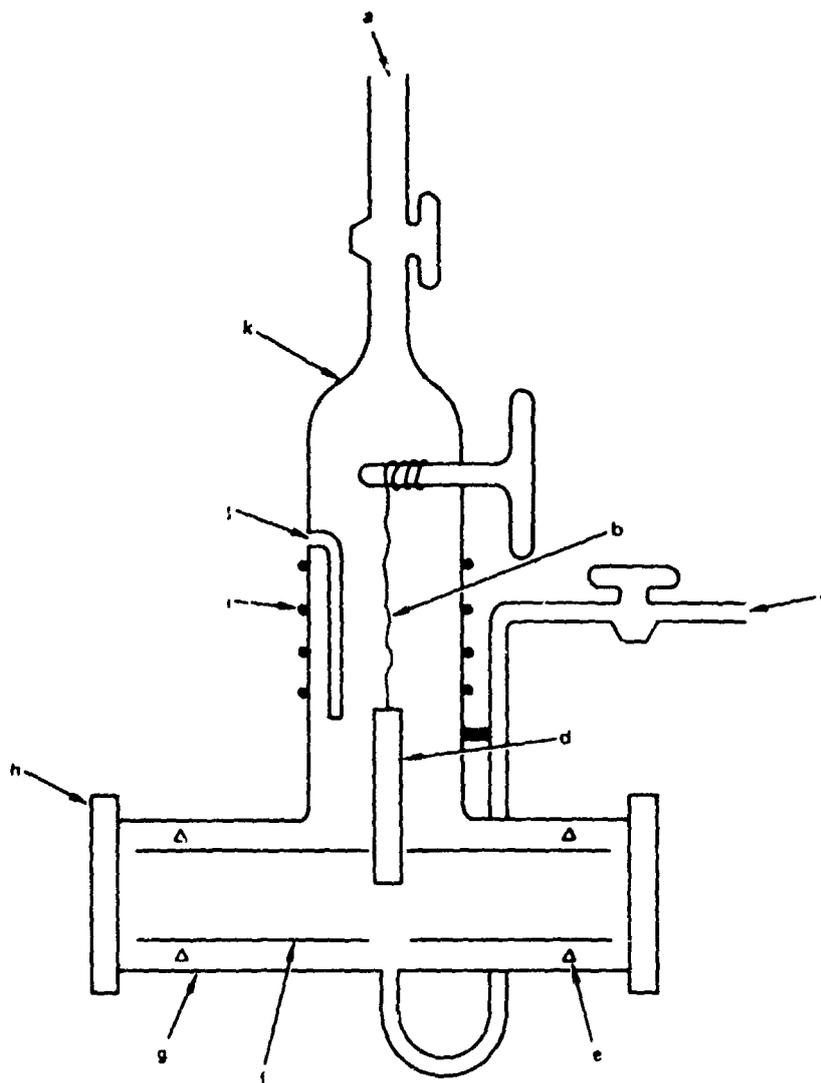
(a)	Gas Outlet
(b)	Pyrex String
(c)	Gas Inlet
(d)	BaF_2 Crystal 8 x 8 x 25 mm
(e)	Teflon Sleeve
(f)	Sample Holder
(g)	Horizontal Section 70 mm x 25 4 mm
(h)	NaCl Window
(i)	Nichrome Heating Wire
(j)	Thermowell
(k)	Vertical Section 130 mm x 21 mm

SA-1945-44

FIGURE 4   THE INFRARED CELL
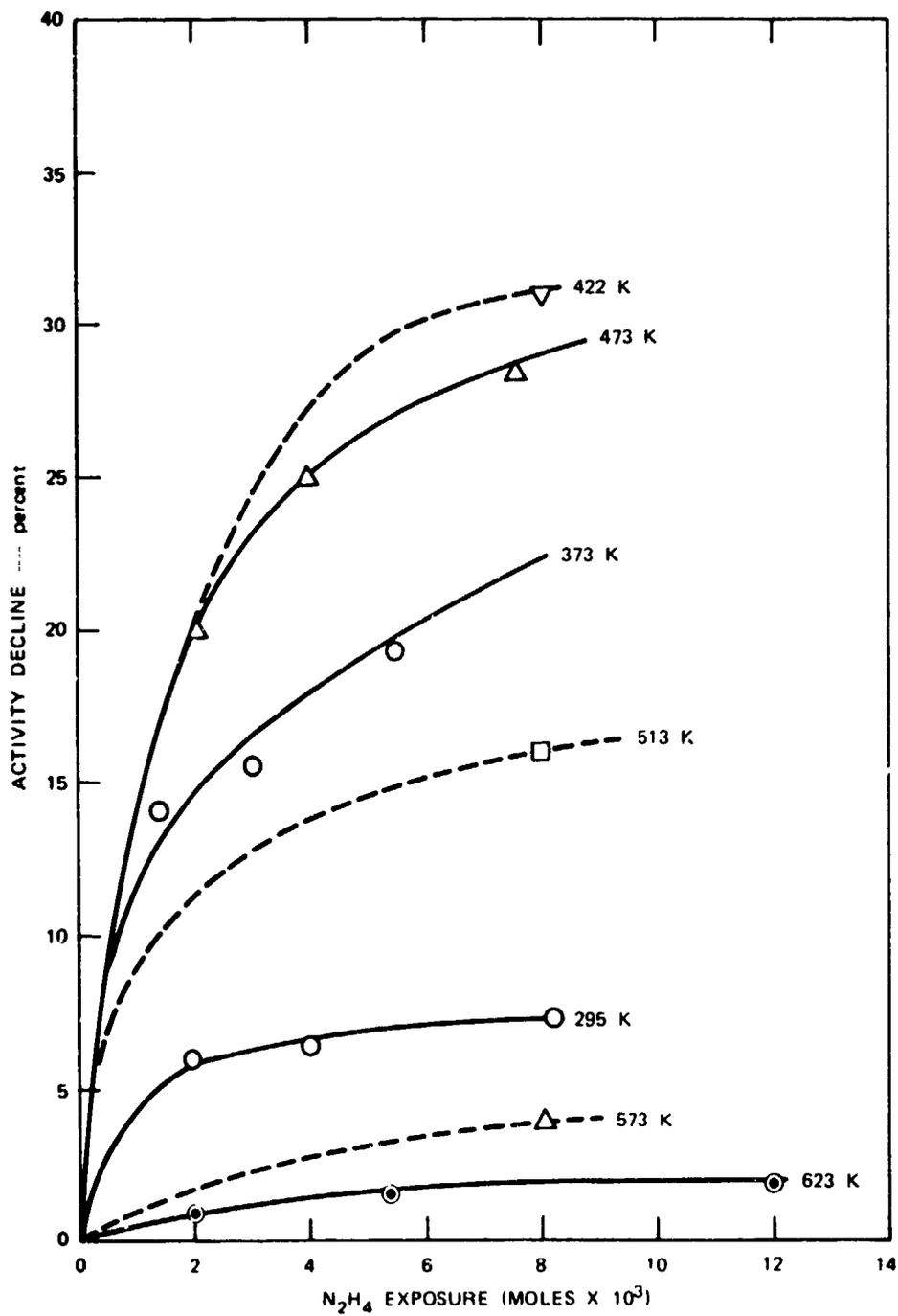
SA-2716 51

FIGURE 5   CATALYST ACTIVITY DECREASE AS A FUNCTION OF TEMPERATURE AND N_2H_4 EXPOSURE $(5.5 \times 10^{-3}g$ 10 wt % $Ir/Al_2O_3)$
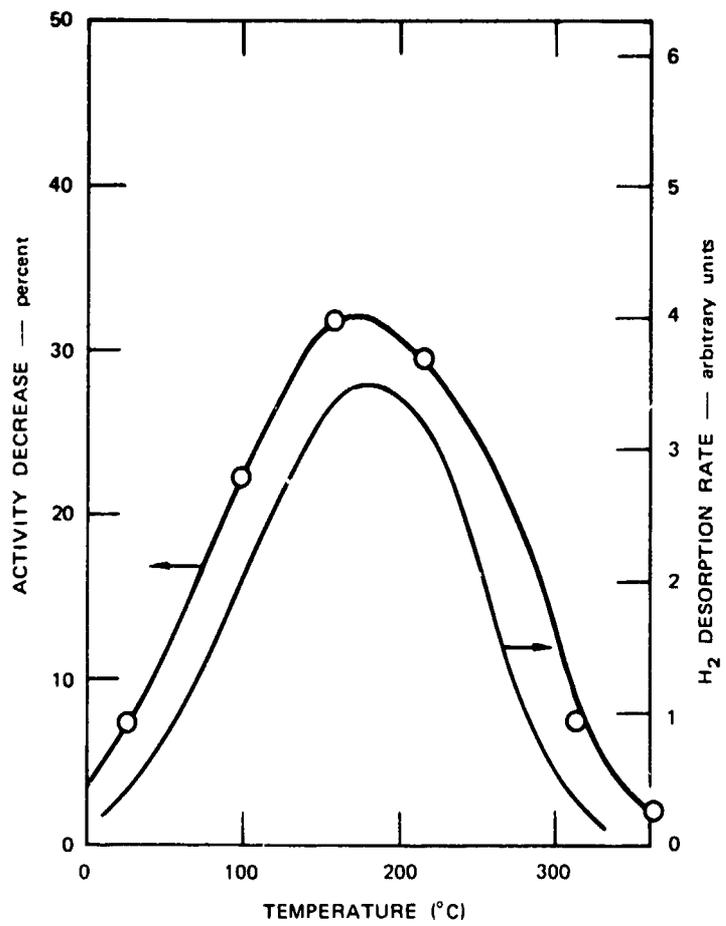
FIGURE 6   CATALYST ACTIVITY DECREASE AFTER EXPOSURE
TO 8.0 X 10^{-3} MOLE N$_2$H$_4$ (10 wt % Ir/Al$_2$O$_3$)
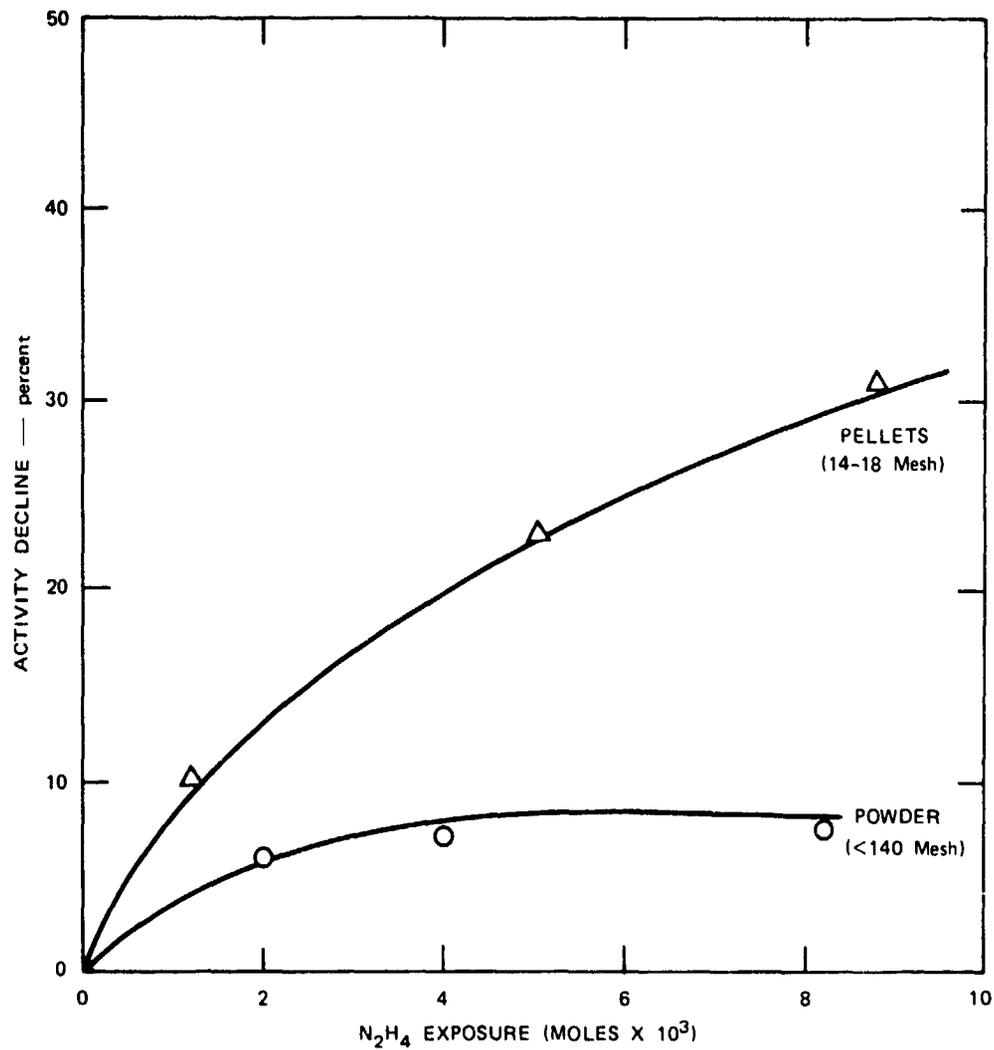
FIGURE 7   EFFECT OF CATALYST PARTICLE SIZE ON ACTIVITY DECLINE AT 298 K
(5.5 mg 10 wt % Ir/Al_2O_3)
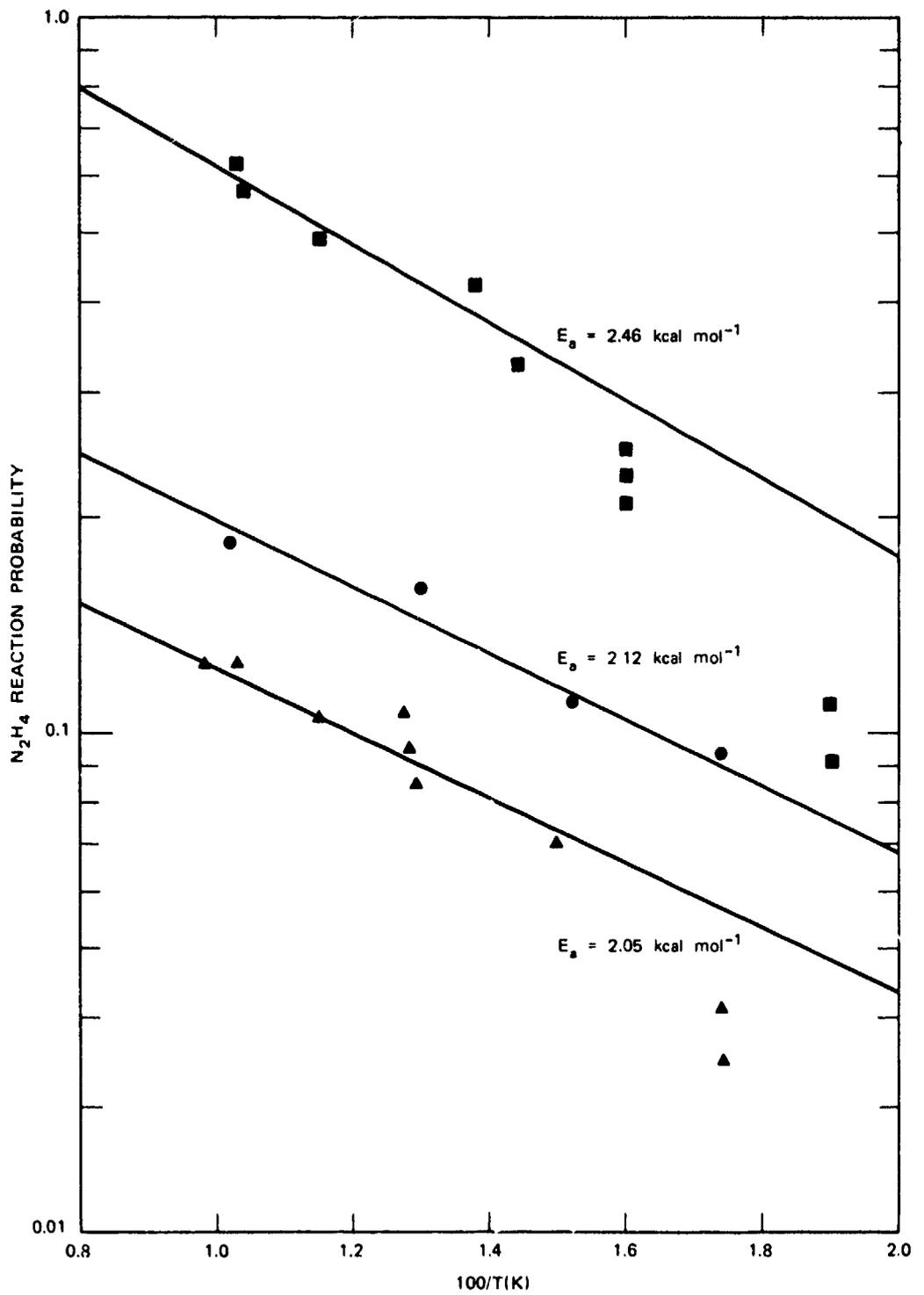
FIGURE 8   ARRHENIUS PLOT OF HIGH-TEMPERATURE N_2H_4 DECOMPOSITION ON SHELL-405

■ Five Average Fresh Pellets from RPL

● Two Large Fresh Pellets from RPL

▲ Five Average Fresh Pellets from RRC
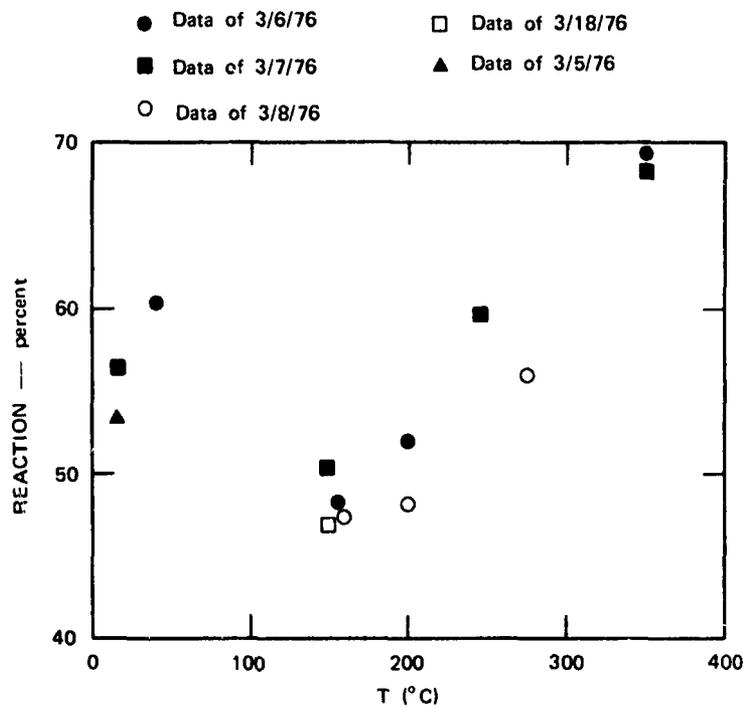
FIGURE 9 REACTIVITY OF ACTIVATED SHELL-405 FOR N_2H_4
DECOMPOSITION

Catalyst activated by heating to 1000 K under H_2 exposure.
Percentage decomposition determined under N_2H_4 flow rate
$\sim 10^{15}$ molec sec^{-1}.
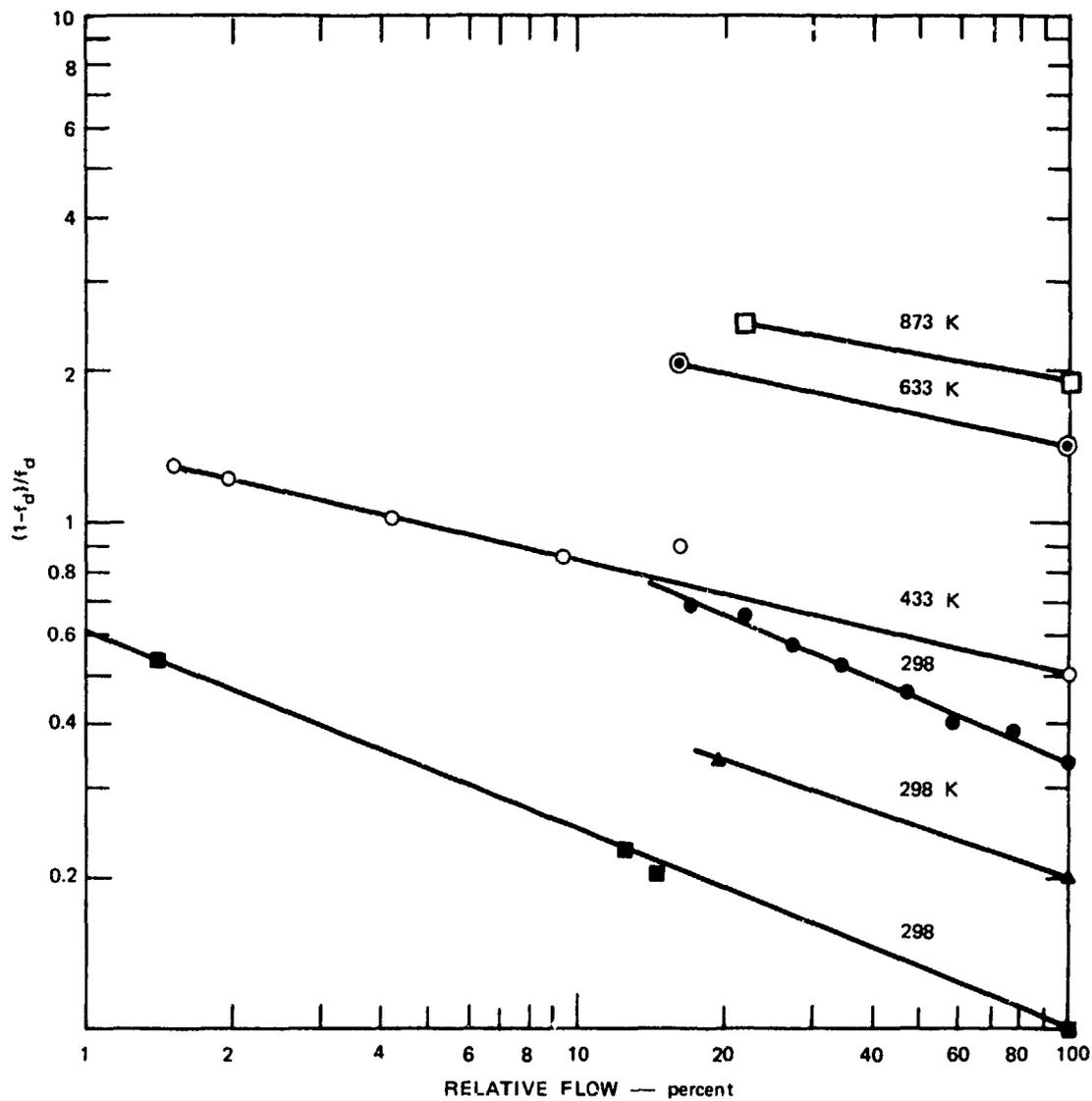
FIGURE 10 MEASURE OF N_2H_4 DECOMPOSITION AS A FUNCTION OF FLOW RATE

O Fresh Catalyst

◉ Fresh Catalyst

□ Fresh Catalyst

▲ Catalyst Partially Poisoned

■ Catalyst Poisoned by Exposure to N_2H_4

● Catalyst Reactivated by Heating to 1000 K with H_2
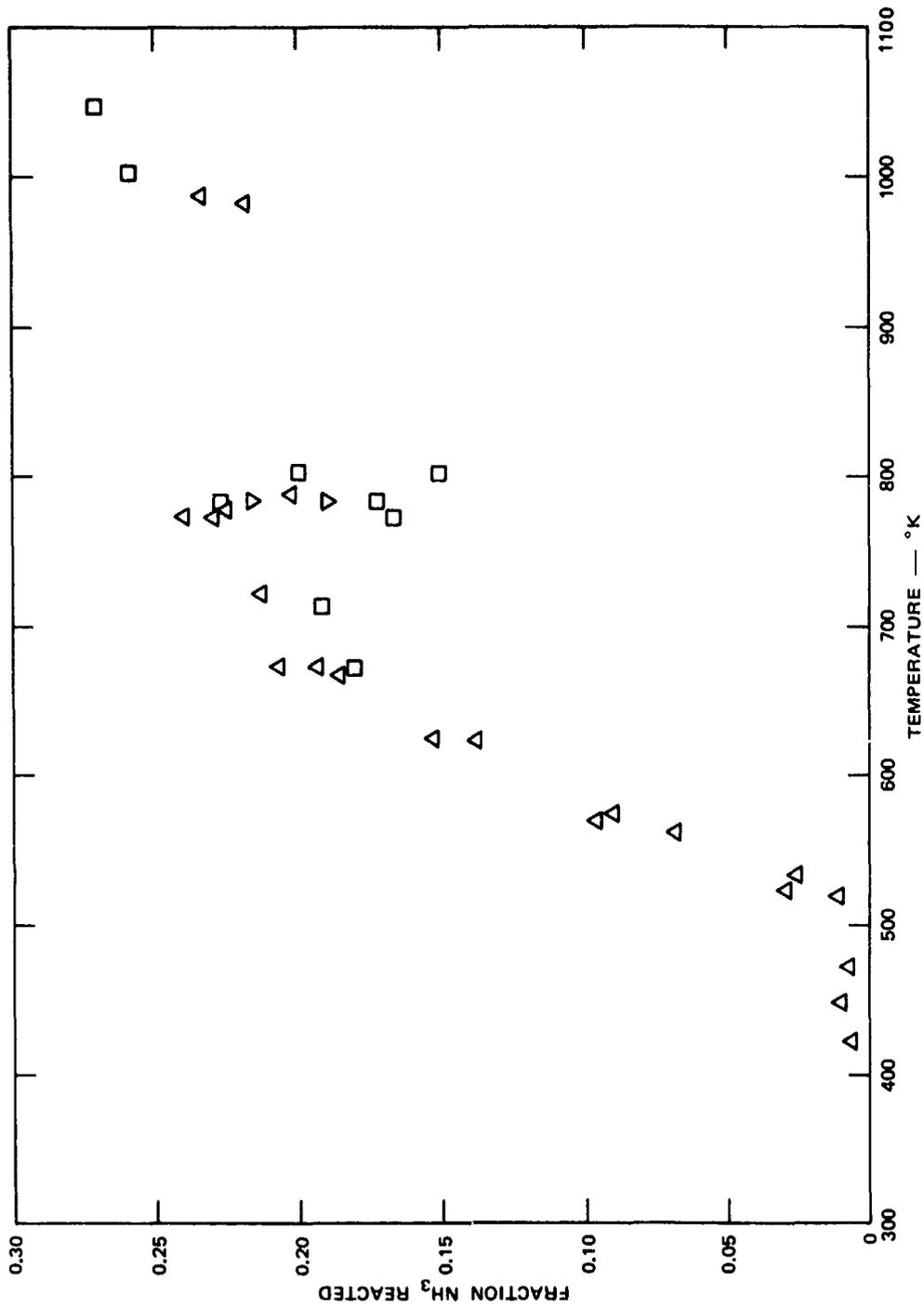
SA-2716-34

FIGURE 11   DECOMPOSITION OF AMMONIA ON FRESH SHELL–405 (32 wt % Ir)

The average number of collisions of a NH_3 molecule with the external surface of shell–405 before escape s ~30 collisions molec^{-1}.   Pressure on NH_3 is ~10^{-3} torr.

Run No. 1 △ ; No. 2 ▽ ; No. 3 □ .
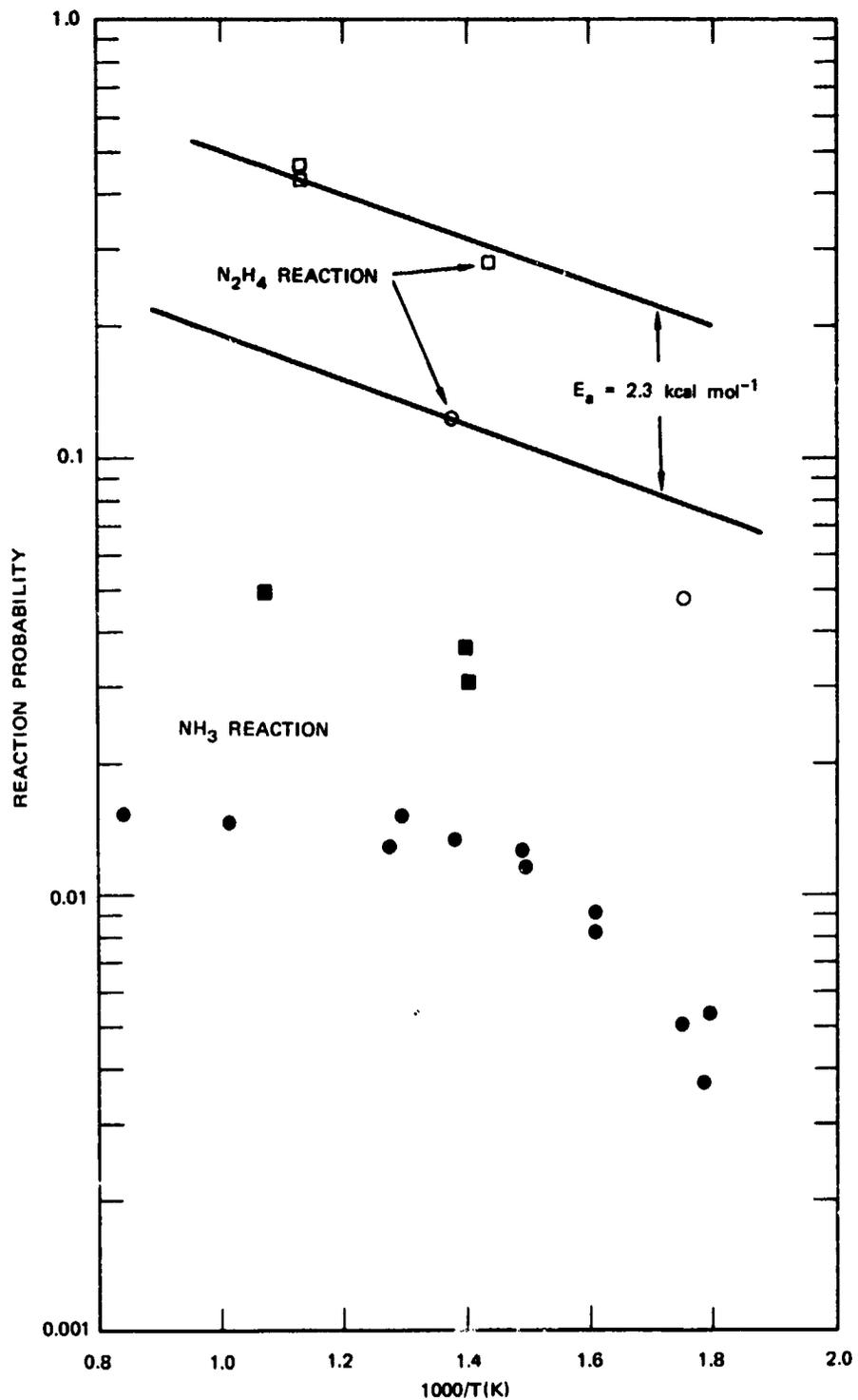
FIGURE 12 COMPARISON OF N_2H_4 AND NH_3 REACTION PROBABILITY ON TWO SAMPLES OF FRESH SHELL-405

Flow $\sim 2 \times 10^{16}$ molecules sec^{-1}

□ ■ N_2H_4 and NH_3, Respectively, Reaction on Six Pellets from RRC

O ● N_2H_4 and NH_3, Respectively, Reaction on Five Pellets from RPL
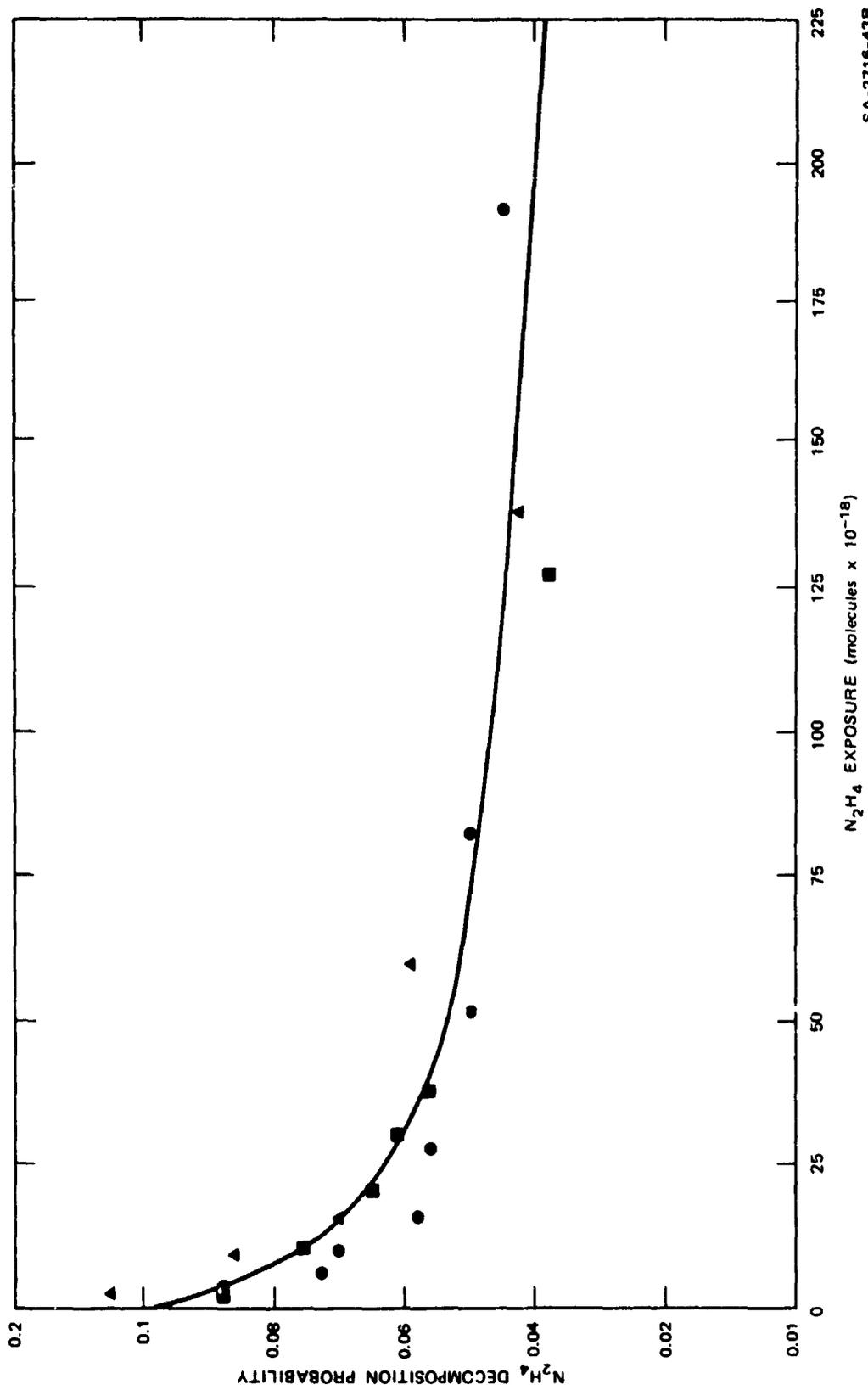
FIGURE 13   REVERSIBLE DEACTIVATION OF SHELL-405 CATALYST RESULTING FROM N_2H_4 EXPOSURE AT 298 K

Catalyst was activated before N_2H_4 exposure by heating in vacuum to 1000 K

N_2H_4 flow = 2×10^{16} molec sec^{-1}

▲ ■ Five Pellets from RPL.   Determinations Separated by 4 Days

● Five Different Pellets from RPL

SA-2716-43R
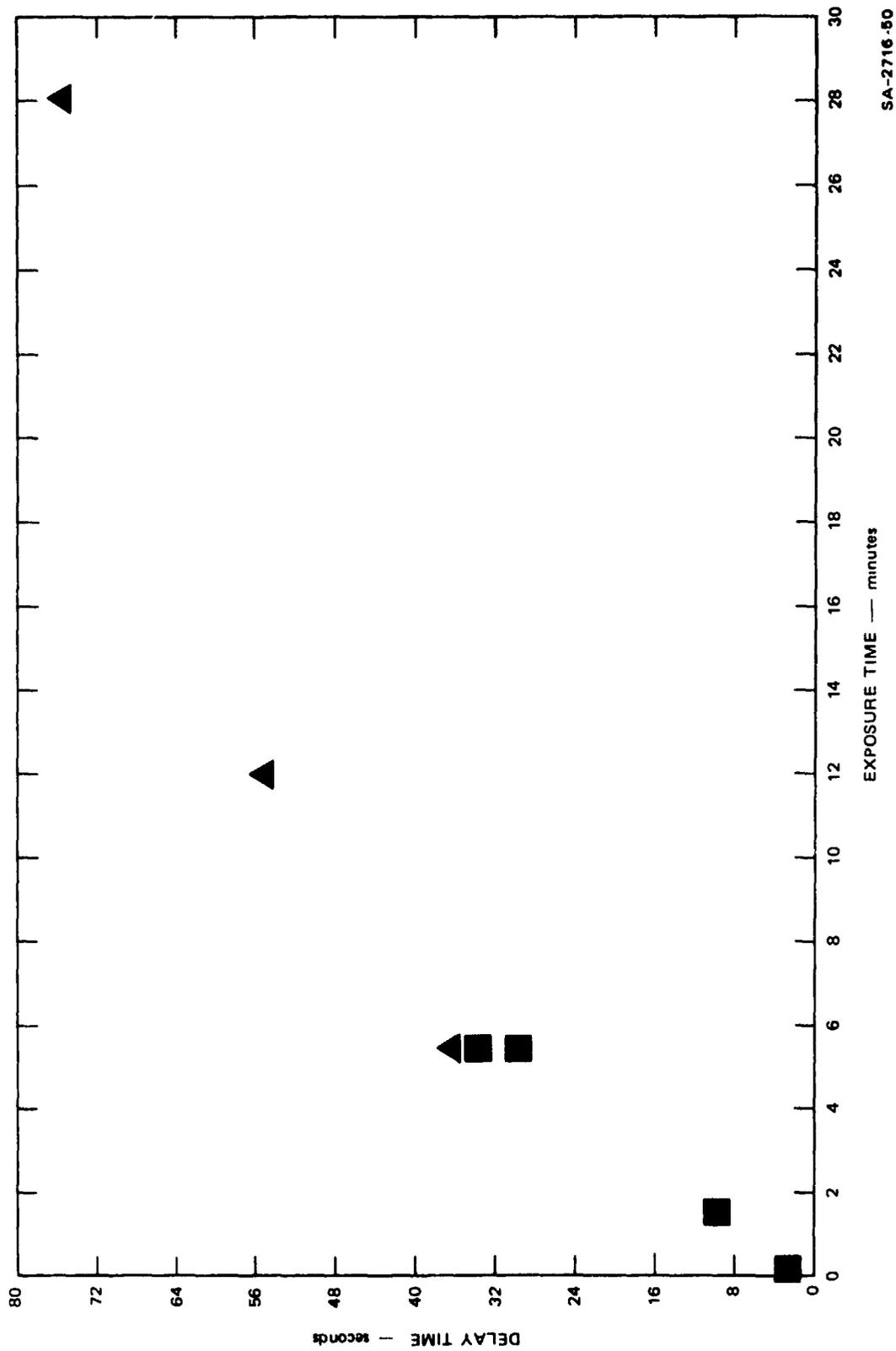
FIGURE 14   EFFECT ON N_2H_4 EXPOSURE ON DELAY TIME

Delay times determined under N_2H_4 flow rate ~10^{15} molecules sec^{-1}
Exposure flow ~10^{17} molecules sec^{-1}

■ Catalyst Activated by Heating to 1000 K Under H_2 Exposure

▲ Catalyst Partially Poisoned

EXPOSURE TIME — minutes

DELAY TIME — seconds
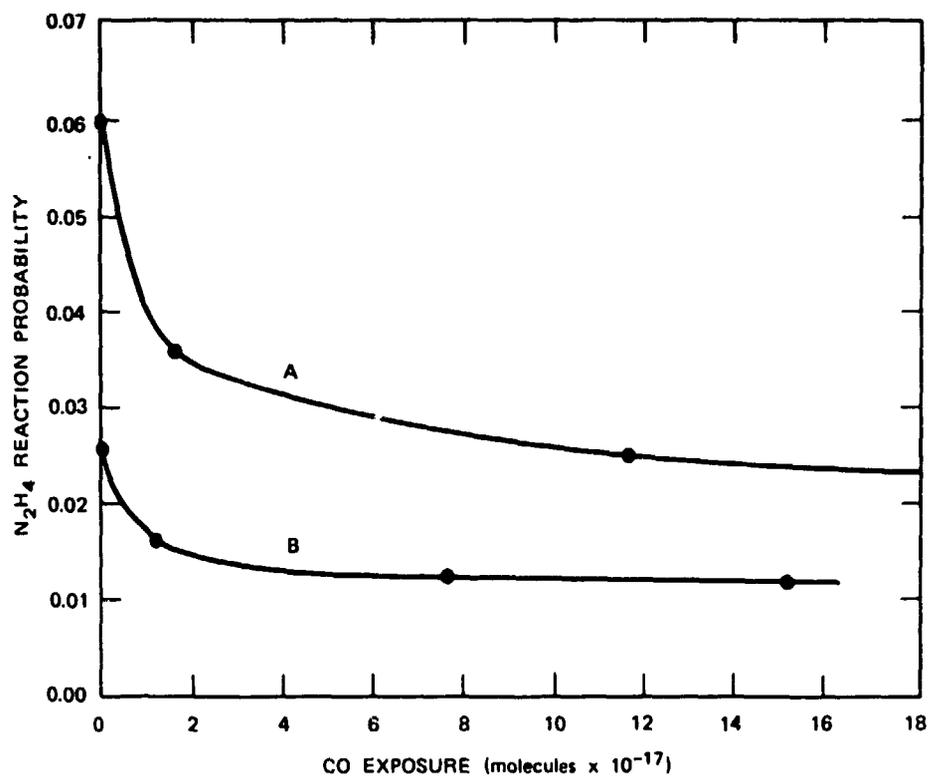
SA-2716-50

SA-2716-44R

FIGURE 15   CATALYST DEACTIVATION BY CO EXPOSURE AT 298 K

A –   Catalyst Activated Before CO Exposure by Heating to 1000 K

B –   Catalyst First Heated to 1000 K and Exposed to N_2H_4 at 298 K
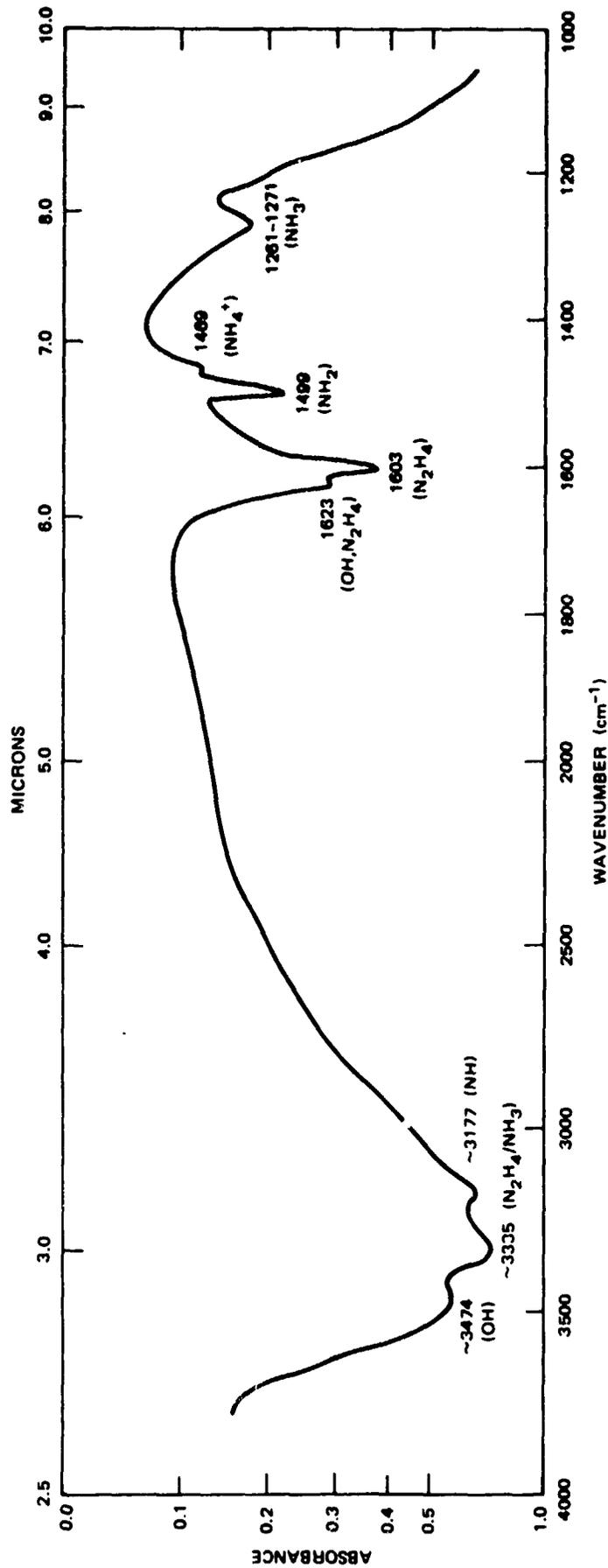
FIGURE 16   INFRARED SPECTRUM OF Ir/Al$_2$O$_3$ EXPOSED TO N$_2$H$_4$ (6.0 X 10^{-3} MOLES)
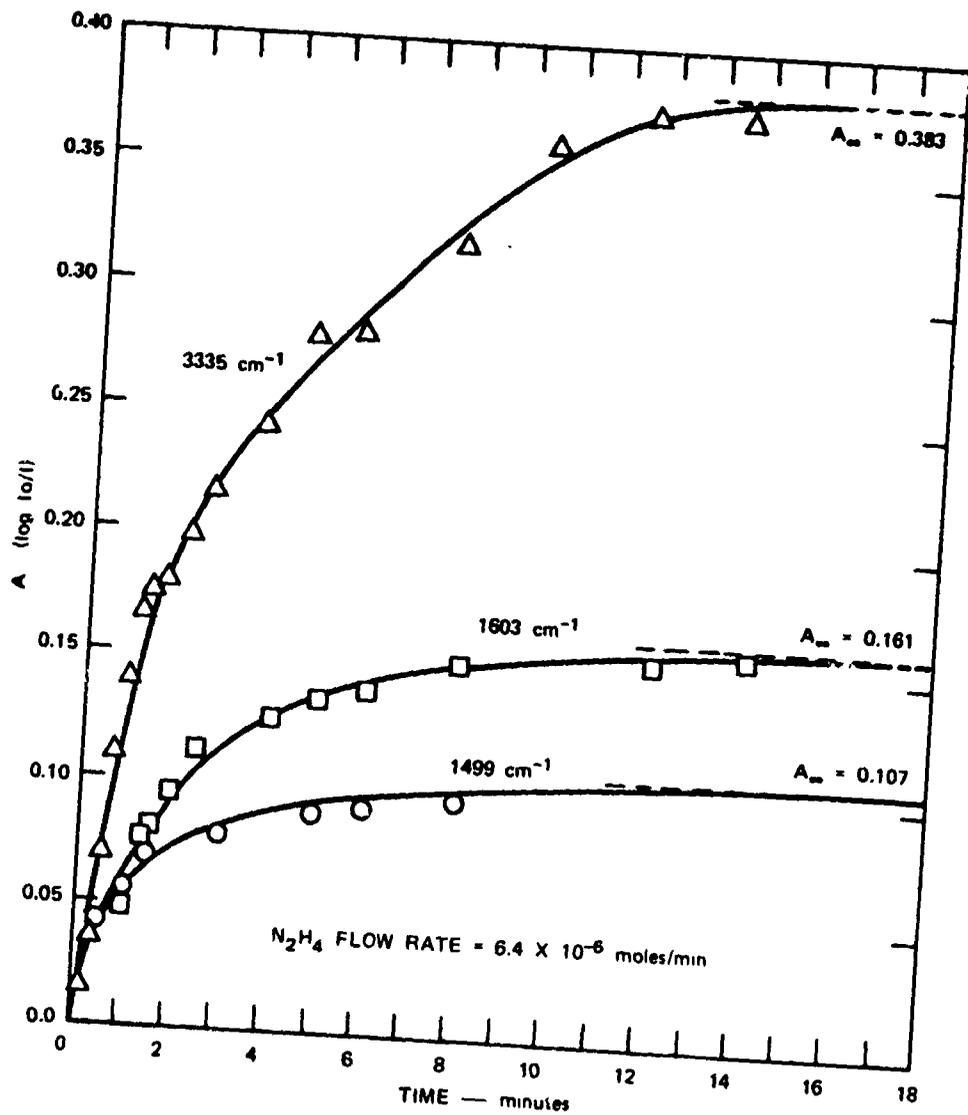
FIGURE 17 FORMATION OF 3335, 1603, AND 1499 cm⁻¹ BANDS ON Ir/Al₂O₃ AS A FUNCTION OF N₂H₄ EXPOSURE
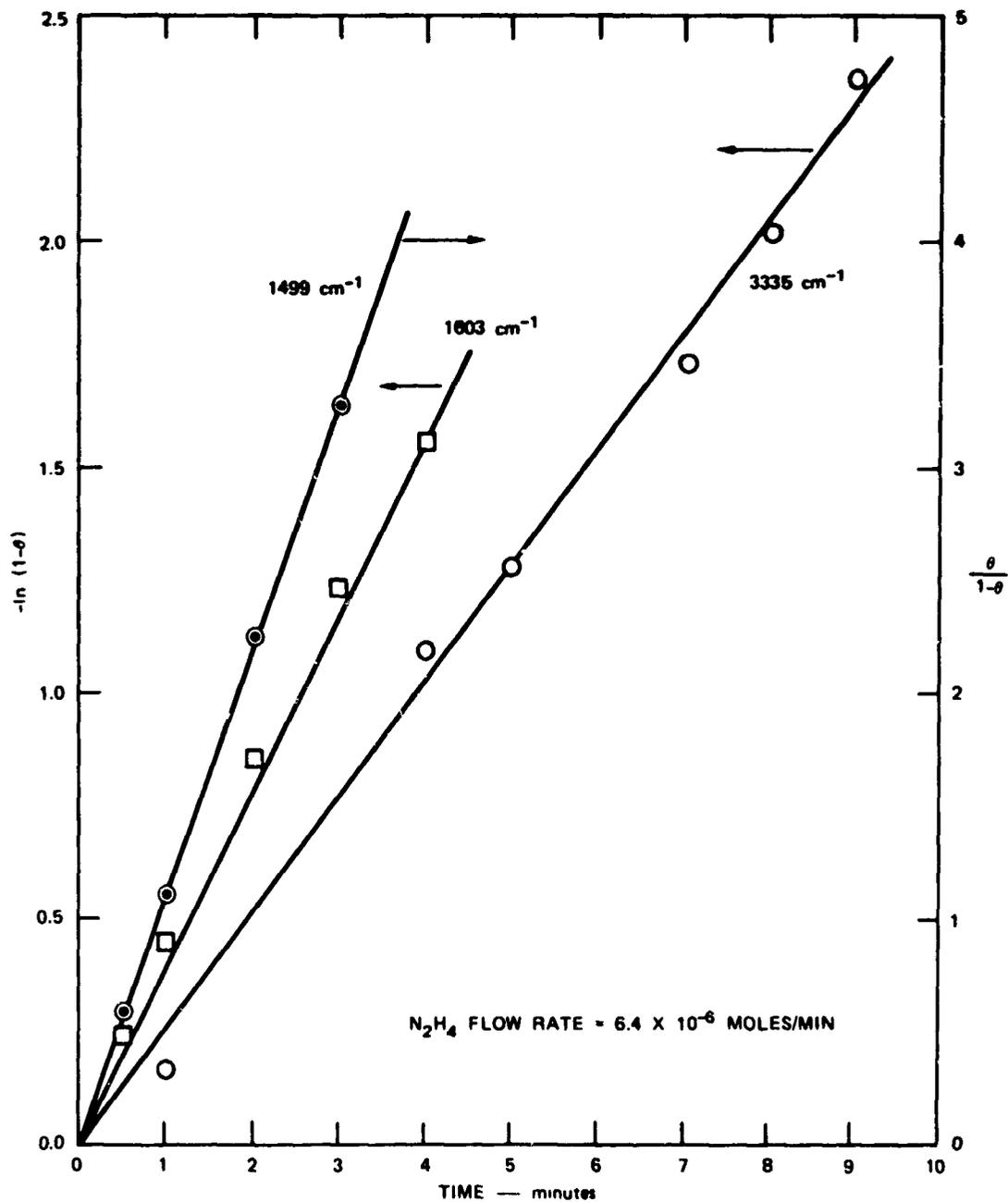
SA-2716-55

FIGURE 18   KINETIC ANALYSIS OF FORMATION RATES OF 3335, 1603, AND 1499 cm^{-1}
BANDS ON Ir/Al$_2$O$_3$ AS A FUNCTION OF N$_2$H$_4$ EXPOSURE
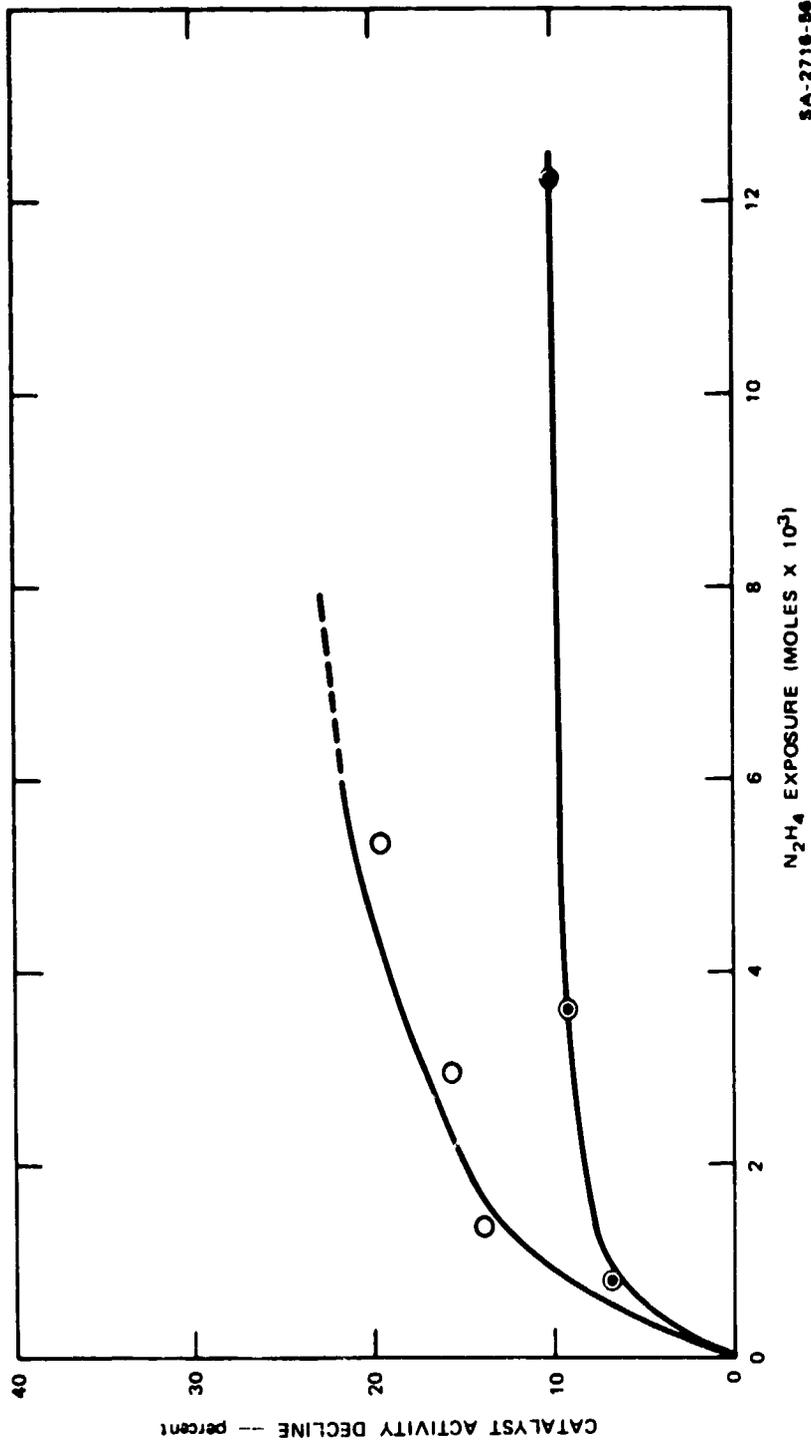
FIGURE 19   EFFECT OF H_2 ON CATALYST DEACTIVATION DURING N_2H_4 EXPOSURE AT 373 K

⊚ 1 vol % N_2H_4/43 vol % H_2/56 vol % He
○ 1 vol % N_2H_4/99 vol % He

45